REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
13-04-2009	Final	10/1/2005 - 9/30/2008

4. TITLE AND SUBTITLE

Potential Energy Surfaces and Dynamics of High Energy Species

5a. CONTRACT NUMBER
FA9550-06-1-0043

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Iowa State University
Ames, Iowa 50011

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR, 875 North Randolph
Suite 325, Rm 3112
Arlington , VA 22203

10. SPONSOR/MONITOR'S ACRONYM(S)
AFOSR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-AFOSR-VA-TR-2016-0659

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Several papers on ionic liquids have been published or submitted as a result of this grant. The first set of papers used second order perturbation theory to study the geometries and substituent effects of the cations commonly employed in energetic ionic liquids. These are variously substituted triazolium, tertazolium, and pentazolium cations. The heats of formation of all species were predicted using G2 and G3 theory. It was consistently found that the most energetic substituents are –CN and $-N_3$. When one cation is combined with one anion, proton transfer almost always occurs with no intervening energy barrier, yielding a neutral pair. When two ion pairs are considered, conceptually similar to the face of a crystal, the ion separated species is predicted to be 6 kcal/mol lower in energy than the double proton transferred neutral species. These calculations were done using coupled cluster theory, but this level of theory is too expensive to study larger clusters. Therefore, we have turned to the fragment molecular orbital method, which can retain the accuracy of full electronic structure theory calculations, while greatly reducing the cost.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*

This is the final report for the High Energy Density Matter (HEDM) grant, FA9550-06-1-0043, "Potential Energy Surfaces and Dynamics of High Energy Species" that ended in Fall 2008.

Ionic Liquids. Several papers on ionic liquids have been published or are in press as a result of this grant:

1. Michael W. Schmidt, Mark S. Gordon, and Jerry A. Boatz, "Triazolium-Based Energetic Ionic Liquids", J. Phys. Chem., A109, 7285 (2005).

The results presented in this paper address several different aspects of energetic ionic liquids. The conclusions reached include the following:

A. The contribution of the two resonance structures in the unsubstituted triazolium cation is roughly equal, with approximately 3/2 p electrons found on both charged nitrogens. Substitution at ring nitrogen atoms produces little change in the extent of this charge delocalization, as shown by both very small geometry changes in the rings, and by MCSCF analysis of the resonance hybrids. The two substituents that cause the most degradation to resonance are CN and NF_2, but to only a small extent. It appears that substitution will not hinder the ability of these cations to form ionic liquids.
B. A number of energetic and less energetic substituents at the ring nitrogens were investigated, and in all cases 1,4 substituted triazoliums are lower in energy than 1,2 substituted triazoliums. There is a small energy preference for monosubstitution at N_1 over N_4 in the 1,4 substituted triazoliums. The heats of formation for substituted gas phase triazolium cations were presented, and the CN substituent is suggested as a synthetic target, over N_3, since the former does not require creating a ring *exo* NN bond, but rather a NC bond.
C. Triazolium dinitramide systems are rich in structure. The numerous geometries and their relative energies are understandable by consideration of hydrogen bonds and protonation energetics. The presence of only small energy barriers, or often, spontaneous transfer of protons from ionic dimers to produce neutral pairs implies that deprotonation is a fundamental mechanism for triazolium decomposition.

2. Deborah D. Zorn, Jerry A. Boatz and Mark S. Gordon, "Tetrazolium-Based Energetic Ionic Liquids", J. Phys. Chem., B110, 11110 (2006).

This work followed the general approach of that in the previous paper. The cyclic structures are generally the lowest in energy for this species; however, the acyclic for is generally not very much higher in energy. The DFT and MP2 energies are generally in good agreement with each other. An MCSCF π orbital analysis indicates that the electrons in the cation ring are delocalized. Calculated heats of formation show that the tetrazolium cation ring has the potential to release large amounts of energy during decomposition and thus has excellent potential as a high energy fuel. This is especially true when the ring is substituted with $-N_3$ or $-CN$. When a cation is paired with oxygen rich anions, a single gas phase ion pair was not generally found to be stable. A proton transfers without barrier from the cation to the anion to form a neutral pair.

3. Ian S.O Pimienta, Sherrie Elzey, Jerry A. Boatz and Mark S. Gordon, "Pentazole-Based Energetic Ionic Liquids: A Computational Study", J. Phys. Chem. A, 111, 691 (2007).

The pentazole cation has nitrogen at all positions on the five-member ring. Ionic liquid dimers composed of the five-membered monosubstituted pentazole cation and the dinitramide, nitrate, and perchlorate anions were investigated in this work. Of the two monosubstituted pentazole cation isomers, it is predicted that the 1,3-isomer is lower in energy than the 1,2-isomer. The relative activation energies and decomposition energies for the decomposition of these cations to N_2 + the corresponding azidinium cation can be related to the electron-donating character of the substituent. An electron-donating substituent tends to increase the activation energy and decrease the decomposition energy. The MCSCF π orbital analysis suggests that the electrons in the cationic pentazole ring are delocalized. The calculated enthalpies of formation show that electron-withdrawing groups such as -CN and $-N_3$ help to increase the heats of reaction. Several dimer structures composed of the H-substituted pentazole and either of the anions mentioned above are proposed and found to be very unstable. The low barrier connecting the ionic and neutral dimers, and the large corresponding exothermicity suggests that a proton is spontaneously transferred to the anion. So, a fundamental step for the decomposition of protonated pentazole is likely to be deprotonation. However, the introduction of additional ion pairs are likely to stabilize the charge separation in the ionic species. It is predicted that the 1-H,2-H-pentazolium-nitrate pair with a barrier for proton transfer of 4.7 kcal/mol is the most stable dimer amongst all of the ion-pairs studied. The ion-pair comprised of the pentazolium cation and perchlorate anion possesses the largest energy content and would have been a desirable high-energy ionic liquid but the 2.7 kcal/mol barrier for proton transfer is prohibitively small for the synthesis and detection of this ionic liquid. The 1-H,3-H-pentazolium-dinitramide pair is more ideal with a relatively larger barrier of 4.5 kcal/mol and a large energy content. Among all the ion-pairs studied, it is calculated that the pentazolium-nitrate pairs provide the largest energy released with a heat of reaction of about 130 kcal/mol.

4. Hui Li, Jerry A. Boatz, and Mark S. Gordon, "Cation-cation Π–Π stacking in small ionic clusters of 1,2,4-triazolium", J. Am. Chem. Soc., 130, 392 (2008).

In this paper, a novel combined MP2/CCSD(T) method was used to illustrate that although, as noted above, single cation/anion pairs tend to spontaneously convert to the corresponding neutral pairs, double cation/anion pairs are significantly more stable than the corresponding neutral pairs. In addition, *ab initio* calculations suggest that cation-cation π-π stacking structures can exist in very small ionic clusters such as two 1,2,4-triazolium cations and two dinitramide or chloride anions. The structure motifs and interaction patterns provide new understanding of ionic materials with aromatic rings. In particular, the presence of two ion pairs appears to function like a face of a crystal, resulting in additional stability.

5. Mark S. Gordon, Jonathan M. Mullin, Spencer R. Pruitt, Luke B. Roskop, Lyudmila V. Slipchenko and JerryA. Boatz, "Accurate Methods for Large Molecular Systems", J. Phys. Chem. (Invited Centennial Feature Article), in press

Three exciting new methods that address the accurate prediction of processes and properties of large molecular systems are discussed. The systematic fragmentaton method (SFM) and the fragment molecular orbital (FMO) method both decompose a large molecular system (e.g., protein, liquid, zeolite) into small subunits (fragments) in very different ways that are both designed to retain the high accuracy of the chosen quantum mechanical level of theory while greatly reducing the demands on computational time and resources. Each of these methods is inherently scalable and is therefore eminently capable of taking advantage of massively parallel computer hardware, while retaining the accuracy of the corresponding electronic structure method from which it is derived. The effective fragment potential (EFP) method is a sophisticated approach for the prediction of non-bonded and intermolecular interactions. Therefore, the EFP method provides a way to further reduce the computational effort while retaining accuracy, by treating the far field interactions in place of the full electronic structure method. The performance of the methods is demonstrated using applications to several systems, including benzene dimer, small organic species, pieces of the alpha helix, water, and ionic liquids.

Cryogenic Species. Timothy J. Dudley and Mark S. Gordon, "Theoretical Study of the Formation and Isomerization of Al_2H_2", Mol. Phys., 104, 751 (2006).

There has previously been considerable interest in embedding small, light metals (such as Al) in solid hydrogen. In this work, the lowest-energy singlet and triplet states of the title molecules were studied extensively. This is the first time that all of the minima on the two surfaces have been characterized at the same, high level of theory – multi-reference perturbation theory. Although the singlet surface is generally lower than the triplet surface at the detected stationary point, the energy difference between the two states is less than 20 kcal/mol. The global minimum on the singlet potential energy surface is the di-bridged isomer, with other singlet isomers lying slightly higher in energy. A purely attractive singlet reaction channel involving the insertion of H_2 into the Al-Al bond of an excited Al_2 species is predicted to be exothermic by ~40 kcal/mol.

MCSCF Hessians. Timothy J. Dudley, Ryan M. Olson, Michael W. Schmidt, and Mark S. Gordon, "Parallel Coupled Perturbed CASSCF Equations and Analytic CASSCF Second Derivatives", J. Comp. Chem., 27, 353 (2006).

Because MCSCF wave functions are very important for many applications, as described in the previous paragraph. In order to characterize electronic states at this level of theory, it is important to have analytic second derivatives, Hessians. MCSCF Hessians are also a key first step in the implementation of non-adiabatic coupling (vibronic coupling) matrix elements which are very important for the study of surface crossings (e.g., in photochemistry). Since MCSCF calculations can be very resource (e.g., time, memory, disk) consuming, it is important to try to reduce these costs. This was accomplished by

developing and implementing the MCSCF Hessians as a parallel code. Good scalability up to 128 processors was demonstrated.

GAMESS. Mark S. Gordon and Michael W. Schmidt, "Advances in Electronic Structure Theory: GAMESS a Decade Later", Theory and Applications of Computational Chemistry, Ch.. 41, C. E. Dykstra, G. Frenking, K.S. Kim, G.E. Scuseria, Eds., Elsevier, 2005.

The electronic structure code GAMESS (General Atomic and Molecular Electronic Structure System) has been supported by AFOSR for ~25 years. In this paper, a description of new developments in GAMESS for the preceding 10 years is presented.

POTENTIAL ENERGY SURFACES AND DYNAMICS OF HIGH ENERGY SPECIES

TOPIC **PAGE**

PROJECT SUMMARY/ABSTRACT
POTENTIAL ENERGY SURFACES AND DYNAMICS OF HIGH ENERGY SPECIES

The **central goals** of the proposed research are to (a) develop efficient and effective methods for electronic structure theory calculations and for interfacing such calculations with dynamics and condensed phase models, and (b) apply these methods to design and evaluate potentially new high energy species. The thermodynamic properties to be predicted are relative isomer energies, heats of formation, and ultimately the specific impulse (I_{sp}). The dynamical properties to be investigated include transition state structures and vibrational frequencies, classical barrier heights, activation energies and free energies, minimum energy reaction paths (MEP's), vibrational frequencies and curvature along the MEP, coupling of the transverse vibrations with the reaction path and with each other, as well as coupling with other electronic potential energy surfaces. The effect of solvation (e.g., exposure to water) and other environmental impacts will be studied with the aid of the effective fragment potential (EFP) model. The specific systems to be explored include ionic liquids and a range of high-nitrogen content and nitrogen-oxygen content species. Polyhedral oligomeric silisesquioxanes are also of interest as protective coatings that are resistant to extreme environments. Many of the proposed studies will involve collaborations with colleagues at the Air Force Research Laboratory and with other HEDM researchers.

An essential ingredient in achieving these goals is our continuing development of parallel electronic structure methods. As implemented in the electronic structure code GAMESS, the speedups attained to date are impressive. Many of the results reported in the previous results section would have essentially been impossible without the availability of parallel GAMESS and the HPC Centers operated by the HPCMO. Further development of parallel methods for correlated wave functions (e.g., energy derivatives for general and state-averaged multi-configurational (MCSCF) and configuration interaction (CI) wave functions, open shell second order perturbation theory), as well as related derivative coupling matrix elements will be very important. Likewise, energy derivatives for the generalized effective fragment potential method and interfaces between EFP and the high-level electronic structure methods will enable the study of environmental effects on HEDM species in both ground and excited electronic states.

STATEMENT OF OBJECTIVES

We will initiate a broad new effort in the field of energetic ionic liquids (EIL). We will focus on both sophisticated electronic structure calculations and on the use of our effective fragment potential (EFP) model in order to bridge the gap between the gas and condensed phase.

Properties of cation monomers. The first step will be to systematically predict the G3 proton affinities for simple amines, $R\text{-}NH_2 + H^+ \rightarrow NH_3R^+$. This simple reaction will provide an initial indication about the inherent ability of a particular substituent to increase the stability of the amino proton and therefore resist proton transfer to the companion anion. The next step will be to optimize the MP2 geometries of the corresponding substituted triazoles and tetrazoles, followed by the prediction of the G3 heats of formation. These calculations will help identify those substituents that are most likely to increase the heat of formation relative to the parent compound. For those substituents that are the most promising, the corresponding di-substitutions will be investigated as well. Although the main interest is in substitution at N, the same substituents will be considered at C as well.

Cation-anion pair interactions. Once the inherent heats of formation as a function of substitution are understood, the next step will be to investigate the ion pair monomers. Therefore, the single ion pair calculations described above will be followed by dimer calculations to determine whether the presence of two cation-anion pairs serves to stabilize the species by, for example, inhibiting proton transfer or charge transfer. Analogous calculations to those described above for the single ion pairs will be repeated for the dimer pairs. Ultimately, the goal is to build a unit cell for each of the most promising species, based on their calculated thermodynamic properties. The potential energy surfaces of these species will provide a first (*ab initio*) step in the study of the condensed phases of these systems

Decomposition and oxidation mechanisms. All of the foregoing analyses focus on structural predictions and thermodynamic quantities for the parent compounds and ion pairs. The next steps will be to initiate investigations of the decomposition and oxidation mechanisms of the cationic and neutral triazole and tetrazole rings.

Extended systems and connection with condensed phase. We will use very high levels of theory to develop accurate potential energy surfaces that can then be used by condensed phase theorists to build reliable potentials with which to perform their simulations. The proposed calculations that are described above are expected to serve in this capacity, in addition to providing important insights in their own right. Second, in order to build potentials that are as reliable as possible, we will develop new efficient, highly scalable methods, so that the most sophisticated methods are applicable to realistic problems on tractable time scales. Third, this group has, over the past several years, been developing a very sophisticated model potential, the effective fragment potential (EFP) that is firmly based in quantum mechanics. The EFP method, when completed, will contain all of the fundamental physics involved in intermolecular, and inter-ionic, interactions. Combined with periodic boundary conditions and either FMM or Ewald sums, the EFP method will allow us to simulate the crystal phase changes, the melting process and subsequent condensed phase behavior, using a combination of Monte Carlo and molecular dynamics methods.

I. Results from Previous Grant Period

A. THEORY/MODEL DEVELOPMENT

Parallel Developments. A highly scalable code for frozen core second order perturbation theory gradients for closed shell molecules has been developed[1] and is on-line for general use at several IBM SP2 and Cray T3E systems, including the T3Es at ERDC, AHPCRC and NAVO and the SP2 at MHPCC. This new code uses the Distributed Data Interface (DDI)[2], so that the large arrays do not have to be replicated. This means that much larger molecules can be studied using geometries based on correlated wavefunctions. The code scales very well for as many as 512 nodes and has already been applied to several challenging compounds. The development of analogous codes for molecules with unpaired electrons, using both spin-restricted and unrestricted wavefunctions, is in progress. The unrestricted second order perturbation theory parallel code under DDI has been completed[3,4] and is now on-line at the same centers. A paper on the restricted open-shell derivation has been published[5], and the development of the parallel code is in progress. A paper on a DDI implementation of the SCF method has also been published[6]. Improved parallel MCSCF codes are under development, and a distributed parallel full CI code has been implemented and a paper published[7]. The multi-reference perturbation theory code (MRMP2) has now been implemented under DDI. The effective fragment potential (EFP) code has been made scalable under DDI[8]. In an important related development, parallel GAMESS now runs on clusters of PCs and Macs (running Linux) and high-end workstations. This is more challenging than self-contained massively parallel computers, since the overhead due to inter-node communications is more complex. This issue has been solved to some extent by using a Gigabit Ethernet switch with large data packets. We are also exploring alternative communications solutions, such as Myrinet, SCI, and Infiniband. These developments and their applications have been enhanced by the construction of a new 32-node, 128-CPU IBM Power3+ cluster using funds provided by a DURIP grant. As for all other GAMESS developments, we will make our experiences in developing scalable clusters available to all users.

Condensed Phase Methods. We have already shown that our effective fragment potential (EFP) method for solvation is excellent for water, in a variety of applications[9]. We are now working on extending the capabilities of the method in several ways. We are exploring several alternative approaches for incorporating dispersion and other higher order terms into the method. Such terms are particularly important for nonpolar solvents. We are also in the process of extending the model so that it is equally applicable and accurate for any solvent. Key to the success will be the derivation of general expressions for charge transfer and dispersion contributions that contain no fitted parameters. This will be very important for our new long-term effort in ionic liquids. The derivation of an expression for the analytic gradient for the EFP-*ab* initio interaction term is in progress. A very important new development (by co-worker Jan Jensen) is a new method for using EFPs across covalent bonds. This will facilitate the representation of large substituents, as well as the treatment of large biological molecules. We have also interfaced the EFP method with two continuum methods, the simple Onsager reaction field and the more

sophisticated polarizable continuum model (PCM)[10,11], and we have very recently developed a density functional theory-based EFP method[12].

As the number of solvent molecules in the system increases, the number of configurations to be considered increases rapidly, and traditional small molecule geometry optimization methods are not effective. We are therefore developing both molecular dynamics and Monte Carlo simulation codes so that the configurational space can be probed more effectively, not only for minima, but for transition states and reaction paths as well. This is also an important first step in the development of methods based on the EFP model for predicting bulk properties and super-critical behavior. We are therefore incorporating Ewald summations into our MD method. Collaborators in this effort are Drs. Paul Day and Ruth Pachter (AFRL)[13]. Related to these dynamical methods is our development and implementation of a method (in collaboration with Prof. Michael Collins, Australian National University) for converting the large numbers of points generated in *ab initio* trajectories into a global potential energy surface, using a modified Shepard interpolation approach.

Major James Shoemaker's Ph.D dissertation in Engineering Physics at the Air Force Institute of Technology focused on the development and applications of an embedded cluster model for treating surface chemistry. Papers on the theoretical method, called SIMOMM, has been published[14,15]. Several papers applying this method have now been published, and a manuscript that describes applications to silicon carbide surfaces has been published[16]. Extensions of this method to metal oxide catalysts are planned. For metals, however, molecular mechanics is not likely to be a viable approach for the bulk, since electrons in such systems are too delocalized. To overcome this problem, we have begun to explore fast multipole methods (FMM) that scale linearly and are also highly parallel, so that the bulk part of the system can be treated by quantum mechanics[17,18].

Other developments . We have also been exploring alternatives and extensions to the popular G2 and G3 methods developed by Pople and co-workers for the accurate prediction of such theormodynamic properties as heats of formation, ionization potentials and electron affinities. One limitation of these methods is that they are applicable only to species that are adequately described by single configuration wavefunctions. This eliminates many transition metal compounds, diradicals and most transition states. We have therefore developed, in collaboration with the Radom group, multi-reference analogs of the G2 and G3 methods[19]. The multi-reference methods are based on CASSCF wavefunctions, instead of Hartree-Fock, followed by multi-reference perturbation theory (instead of MP2) and finally multi-reference CI.

Since NMR properties are a very important experimental diagnostic, both in the gas phase and in solution, we are in the process of developing methods and codes for predicting NMR properties. Two recent accomplishments are the derivation for the computation of NMR coupling constants at the multi-reference perturbation level of theory[20] and the derivation, implementation and first successful application of a method to calculate NMR chemical shifts in the presence of effective fragment potentials[21].

B. APPLICATIONS

POSS Compounds. Polyhedral oligomeric silsesquioxanes (POSS) have a wide variety of important applications, including lubricants and coatings. They are also resistant to extreme environments. Consequently, there is considerable interest in these species in industry, universities and Air Force Laboratories. We have therefore initiated a detailed study of POSS compounds, with primary emphasis on the mechanisms by which these species form, in both the gas phase, and in solution and the presence of catalysts. In the first series of calculations, we examined the three stepwise hydrolysis steps of trichlorosilane, followed by the condensation of the product trihydroxysilane. All four reactions are predicted to have large barrier heights in the gas phase, but the addition of just one extra water molecule is sufficient to reduce all barriers to zero or nearly zero, except for the first hydrolysis step. In the latter, there is still a residual barrier of almost 10 kcal/mol. So, the next step will be to examine the effect of additional water molecules, especially on this first step.

Calculations have also been completed on the next steps in the mechanism, in which the initial condensation products, disiloxanes, are further condensed to the ring compounds D3 and D4[22]. These results are consistent with those reported above, in that initially high barriers are reduced to nearly zero by an additional water molecule. The most recent effort has been the study of the addition of more water molecules, which lower barriers even further, and analysis of substituent effects on the reaction mechanism and energetics[23].

Although our main focus is on Si-based POSS, the Ti analogs are also of interest. We have therefore initiated a series of calculations on the Ti-POSS compounds to study their properties[24]. These mixed Si-Ti POSS also have potential as catalysts, and a paper of the efficacy of these potential catalysts has been published[25].

Three dimensional cage compounds, including zeolites, have been of interest as a possible means for separating small gas molecules. In collaboration with Dr. Shawn Phillips (AFRL-Edwards) we have therefore completed a series of calculations in which the potential energy surfaces for passing N_2 and O_2 through the faces of T_n, n = 8, 10, 12[26]. For T_8, both the energy barriers and the endothermicities are very large for both N_2 and O_2. In both cases, electron correlation is essential for an adequate estimate of the energetics. For N_2, the barrier height is on the same order as the SiO bond strength, while the O_2 barrier is much smaller. Despite these observations, the SiO bond does not break upon entry of either molecule, and the species with the endohedral gas molecules are minima on their respective potential energy surfaces. As the size of the cages increases, the barriers and endothermicities decrease as one would expect.

Fuels with High N-Content. There has been considerable interest in the last several years in the potential for cubic molecules as high energy fuels. Cubane itself has been considered, and so far rejected because of the complexity of its synthesis. The octasila analog of cubane has been prepared. Unlike the carbon system, the cubic structure is the most stable Si_8H_8 isomer. This makes it potentially very interesting, since it is still rather

high in energy. However, the heavy mass of Si precludes any viability of such species as high-energy fuels[27].

On the other hand, cubic N_8 is a light, very high energy fuel that has been the subject of considerable attention. Extensive calculations, however, illustrate that the upper limit of the barrier separating this species from four nitrogen molecules is 20 kcal/mol. It is, therefore, not a viable high energy fuel. In the process of studying the cubic N_8 potential energy surface, it was discovered that there are three N_8 isomers that are much lower in energy than the cube, yet still much higher in energy than molecular nitrogen. The potential energy surfaces for these isomers have now been studied in detail. Two of these have barriers on the order of 15-20 kcal/mol (too small), but the third has a barrier of nearly 30 kcal/mol. So, this isomer may be a viable synthetic target[28].

Related to the foregoing, much attention has been paid recently to N_4 as a potential fuel. Many references are made to a barrier on the order of 50-65 kcal/mol, even though it has been shown by Yarkony that non-adiabatic interactions reduce this barrier to less than 40 kcal/mol. For the first time, we have mapped out the potential energy surface that leads from tetrahedral N_4, using second order perturbation theory. One also must consider the possibility that two N_4 molecules could interact and form molecular nitrogen. This possibility is being explored in this laboratory.

Christe and co-workers at AFRL (Edwards) have isolated the first new all-nitrogen species in nearly a century. With the counter ion, this species is $[AsF_6^-][N_5^+]$. We have now studied the potential energy surface of this species as it forms $AsF_5 + FN_5$, and subsequently the pathway leading from FN_5 to $FN_3 + N_2$. A paper describing this work has recently been published[29]. Another paper on the possibility of making crystals of N_5^+/N_5^-, has also been published[30]. Both of these latter papers have been done in collaboration with colleagues at AFRL-Edwards.

There has been considerable experimental and theoretical interest in metal-doped solid hydrogen. We have an ongoing series of investigations of the low-lying electronic states of BH_2 system, to determine the energetics by which the metal is held as a weakly bound species in the matrix and the ease with which two metal atoms find each other. Similar studies are under way on the B_2-H_2 and Al_2-H_2 systems.

The desired reaction product for burning Al-doped H_2 is Al_2O_3, since it is the thermodynamically most stable aluminum oxide. However, it is unknown how or when this species forms in the process. We have therefore initiated an extensive study of the potential energy surface that leads from Al and O_2 to various oxides[31,32].

II. PROPOSED RESEARCH

A. APPLICATIONS

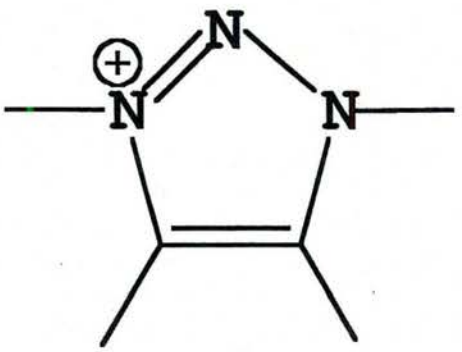
Ionic Liquids. We will initiate a broad new effort in the field of energetic ionic liquids (EIL). This effort, outlined in detail in the following paragraphs, will involve

collaborative efforts with several colleagues, including Drs. Boatz, Mills, Drake, and Hawkins (AFRL-Edwards) and Professors Thompson (Oklahoma State) and Voth (Utah). Since the issues involving EIL range from fundamental questions of bonding, kinetic stability and thermodynamics to condensed phase issues such as phase transitions, melting, viscosity and surface tension, it is critical that we interface with both theoretical and experimental colleagues in order to make optimal progress.

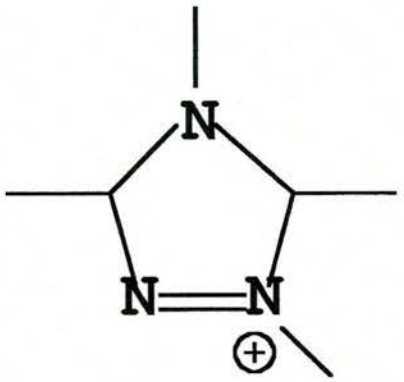
Requirements for a viable EIL include:

1) A cation that has a large, positive heat of formation, in order to produce as large an I_{sp} as possible, and that has as low a melting point as possible.
2) A companion anion that can act as an oxidizer.

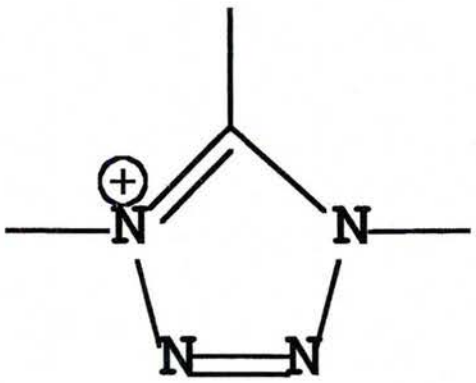
Therefore, much of the recent focus has been on cyclic nitrogen containing cations, such as triazoles and tetrazoles, and oxygen containing anions:



1,2,3-triazoles



1,2,4-triazoles



Tetrazoles

Acyclic cations are also a possibility, but the strain in 5-membered rings tends to increase the heat of formation, and aromatic character can stabilize the ring sufficiently to make synthesis feasible. In general, asymmetry in the ring is desirable, since this seems to lower the melting point, a desirable property. Delocalization of the ionic charge is also desirable. Target anions include simple ones such as NO_3^-, ClO_4^-, and $N(NO_2)_2^-$ (dinitramide), as well as more complex ones like $NClO_3^{-2}$, $B(NO_3)_4^-$, $B(ClO_4)_4^-$, $Al(NO_3)_4^-$. Oxygen-free anions such as N_3^- and N_5^- are also of interest.

We will focus on both sophisticated electronic structure calculations and on the use of our effective fragment potential (EFP) model in order to bridge the gap between the gas and condensed phase. The former will be in collaboration with Dr. Boatz, while the latter will rely on input from and interactions with Professors Thompson and Voth. Specific efforts are summarized in the following projects. Details regarding theoretical approaches are presented in Section B.

Properties of cation monomers. The first step will be to systematically predict the G3 proton affinities for simple amines, $R\text{-}NH_2 + H^+ \rightarrow NH_3R^+$. This simple reaction will provide an initial indication about the inherent ability of a particular substituent to increase the stability of the amino proton and therefore resist proton transfer to the companion anion. Throughout this discussion, the R groups of interest will include NO_2, N_3, NH_2, CN, CH_3, NF_2, CF_3, OH, F, C_2H_3, OCH_3. The next step will be to optimize the MP2 geometries of the corresponding substituted triazoles and tetrazoles, followed by the prediction of the G3 heats of formation. These calculations will help identify those substituents that are most likely to increase the heat of formation relative to the parent compound. For those substituents that are the most promising, the corresponding di-substitutions will be investigated as well. Although the main interest is in substitution at N, the same substituents will be considered at C as well.

Cation-anion pair interactions. Once the inherent heats of formation as a function of substitution are understood, the next step will be to investigate the ion pair monomers. The important questions regarding these simple ion pairs are

(1) What are the relative energies of the ion pairs relative to the separated ions?

(2) Is there significant charge transfer upon ion pair formation, or do the ions retain their distinct ionic character?

(3) For those species in which proton transfer from cation to anion is possible, does it occur spontaneously? If not, how large is the barrier for proton transfer? How large is the barrier for transfer of the R-(N) group from cation to anion? What are the relative energies of ion pairs vs. neutral pairs?

Monomer ion pairs do not necessarily reflect the behavior of ionic liquids in the condensed phase. Therefore, the single ion pair calculations described above will be followed by dimer calculations to determine whether the presence of two cation-anion pairs serves to stabilize the species by, for example, inhibiting proton transfer or charge

transfer. Analogous calculations to those described above for the single ion pairs will be repeated for the dimer pairs. Ultimately, the goal is to build a unit cell for each of the most promising species, based on their calculated thermodynamic properties. The potential energy surfaces of these species will provide a first (*ab initio*) step in the study of the condensed phases of these systems. The latter, discussed in more detail below, will be performed in collaboration with colleagues (Thompson, Voth) who are expert in this field.

All of the geometry optimizations described here will be performed using second order perturbation theory and reliable basis sets. For the smallest species, the new coupled cluster codes recently implemented in GAMESS[33] will be employed to test the MP2 relative energies. Companion calculations will be performed with the B3LYP density functional theory approach, in order to assess the viability of this approach. The B3LYP calculations are less time-consuming and therefore may be an attractive alternative for larger ion pair clusters.

Decomposition mechanisms. All of the foregoing analyses focus on structural predictions and thermodynamic quantities for the parent compounds and ion pairs. The next step will be to initiate an investigation of the decompositions of the triazole and tetrazole rings. Since it is not known whether these decompositions occur before or after proton (or substituent) transfer, both possibilities will be investigated. Clearly, it is not possible to know beforehand exactly what decomposition mechanisms will most viable, however, the following general approach seems sensible:

(1) Unimolecular decompositions of the cationic and neutral ring compounds will be studied. Extrusion of a very stable N_2 moiety seems most likely, especially for the neutral, unsubsituted rings. Substitution at various positions on the rings is likely to alter the relative stabilities of various breakdown products. Barrier heights, minimum energy paths (MEPs), and ultimately dynamic reaction paths (DRPs)[34] will be calculated as a function of substituent. The DRP approach (essentially an *ab initio* semi-classical trajectory on-the-fly, combined with an RRKM prediction of lifetimes, was particularly useful in our analysis of the FN_5 decomposition modes[29]. A DRP can be performed with any level of theory in GAMESS, and the availability of scalable analytic gradients for MP2, MCSCF, and DFT makes the process rather efficient. The first step in this phase of the investigation will be to study the parent ring compounds. This will provide the baseline against which the effects of substituents can be measured. Then, those substituted compounds that are most promising, based on the earlier thermodynamic studies and guidance from our experimental colleagues, will be investigated.

(2) It is clearly very important to analyze the potential energy surfaces for the oxidation of the cation by the negatively charged, oxygen-containing counter ions. Many oxidation processes are possible for each ring, and the presence of substituents may very well alter the mechanisms dramatically. As for the unimolecular decompositions, the first step will be to study the competing oxidation mechanisms for the unsubstituted compounds, with an emphasis on the processes that are likely to either have the lowest barriers or the most stable oxidation products (or both). Since it is not known at what stage the oxidation

occurs, both the ionic and neutral species will be studied, using the same computational methods as those described above. By this point in the project, we will have learned a great deal about the effects of substituents on the thermodynamic and unimolecular decomposition processes. Our approach to the oxidation mechanisms for the substituted compounds will be guided by this gained understanding and, as always, by our experimental colleagues. Since there is currently very little quantitative experimental data about these processes, it is important to keep in mind that a solid qualitative overview, especially of the effects of substitution, may be as useful as detailed quantitative comparisons.

(3) It is also important to investigate the impact of heterogeneous catalysis on the decomposition mechanisms and energetics. The important catalysts are Pt, Pd, Ni, and Ir. The analysis of heterogeneous catalysis on these metals will be accomplished in increasingly complex stages. Since the active sites for catalysis are likely to be relatively small clusters of metals, the first step will be to systematically re-examine the unimolecular decomposition and oxidation mechanisms in the presence of small metal clusters. This will provide us with an initial glimpse into the manner in which these mechanisms are altered by the presence of the catalyst. We are currently in the process of developing two-dimensional periodic boundary conditions for the study of surface science, especially heterogeneous catalysis, on metal surfaces using the fast multipole method (FMM) developed already for both the Hartree-Fock and DFT levels of theory[17,18], and extensions of this approach to both MCSCF and MP2 are planned (see Section B below). Therefore, in the longer term this approach will facilitate the analysis of the heterogeneous catalysis of the decomposition of ionic liquids for the "infinite" systems.

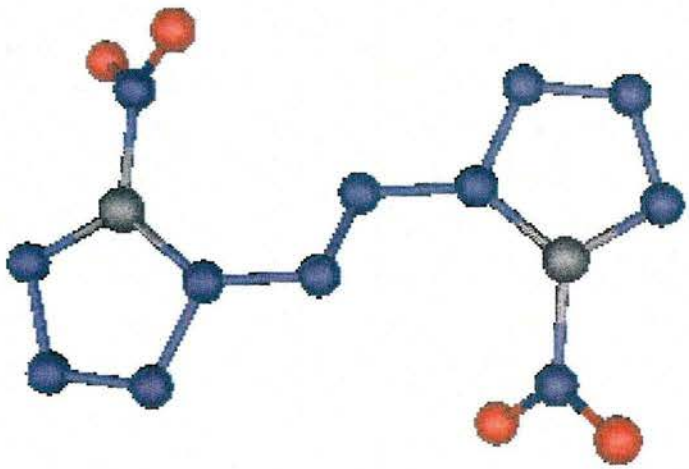
Extended systems and connection with condensed phase. There are several ways in which an electronic structure theory group can contribute to an understanding of condensed phase phenomena. One is the use of very high levels of theory to develop accurate potential energy surfaces that can then be used by condensed phase theorists to build reliable potentials with which to perform their simulations. The proposed calculations that are described above are expected to serve in this capacity, in addition to providing important insights in their own right. Second, in order to build potentials that are as reliable as possible, it is also important to develop new efficient, highly scalable methods, so that the most sophisticated methods are applicable to realistic problems on tractable time scales. Several such proposed developments are discussed in Section B. Third, this group has, over the past several years, been developing a very sophisticated model potential, the effective fragment potential (EFP) that is firmly based in quantum mechanics. Described in detail in Section B, the EFP method, when completed, will contain all of the fundamental physics involved in intermolecular, and inter-ionic, interactions. Combined with periodic boundary conditions and either FMM or Ewald sums (both of which will be coded), the EFP method will allow us to simulate the crystal phase changes, the melting process and subsequent condensed phase behavior, using a combination of Monte Carlo and molecular dynamics methods. This will be accomplished in collaboration with Professor Thompson. The EFP capability goes well beyond that of a sophisticated model potential. It is interfaced with the fully QM capabilities in GAMESS,

so that it can also function as a QM/MM method. For the study of ionic liquids, this means one can insert a QM "solute" such as a single ion pair (for example) into the "bulk" represented by EFPs and then study any of the reaction mechanisms discussed in the preceding paragraphs. This will extend our understanding of these systems well beyond the small clusters.

Note that the calculations described in the previous paragraphs will be very demanding. Their success will be facilitated by the continuing development of the parallel code in GAMESS (See Section IIB) and continuing access to the DoD Major Shared Resource Centers.

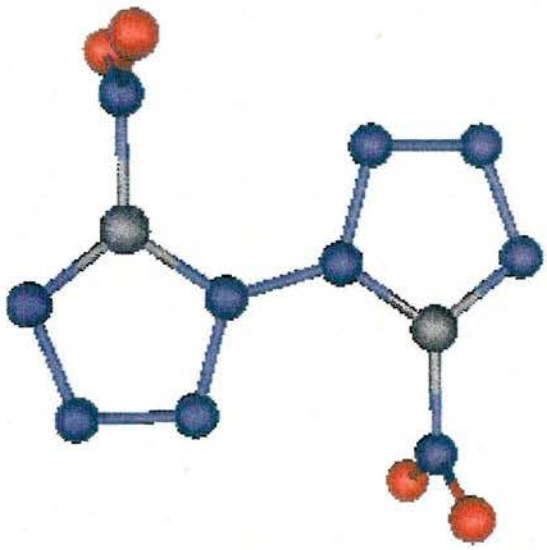
Polynitrogen species. We have initiated an ongoing collaboration with experimental colleagues at SRI International (the late Rob Schmitt and Jeff Bottaro) to investigate the viability of a number of polynitrogen compounds as monopropellants. The general approach is to first estimate the heat of formation of each species using variants of the G2[35] and G3[36] methods developed by Pople and co-workers. These methods make use of approximate additivity of correlation and basis set corrections to obtain thermodynamic properties to within a few kcal/mol. For molecules of the size of those of interest here, these are very demanding calculations and require the use of parallel computers and the parallel electronic structure codes developed in our laboratory (see Section B below). Once a reliable heat of formation is available, colleagues at AFRL-Edwards (Jerry Boatz and Jeff Mills) calculate the specific impulse, I_{sp}. If the I_{sp} seems to be viable, one then must consider possible decomposition processes, including unimolecular decomposition and attack by obvious environmental species, such as N_2, O_2, and water.

The initial focus in this phase of the research has been on compound **1**, shown below.



1

Using a combination of isodesmic reactions and the G2 model on the IBM SP2 at the Maui High Performance Computation Center, the heat of formation for **1** is predicted to be 456.8 kcal/mol. This translates to an I_{sp} of 240 sec, compared with 230 sec for hydrazine. So, this appears to be a very promising fuel. However, it is always important to consider the stability of such high energy species to various reactions, before asserting their viability as fuels. One possible reaction is the loss of molecular nitrogen from the center of **1** to form the smaller species **2** shown below:

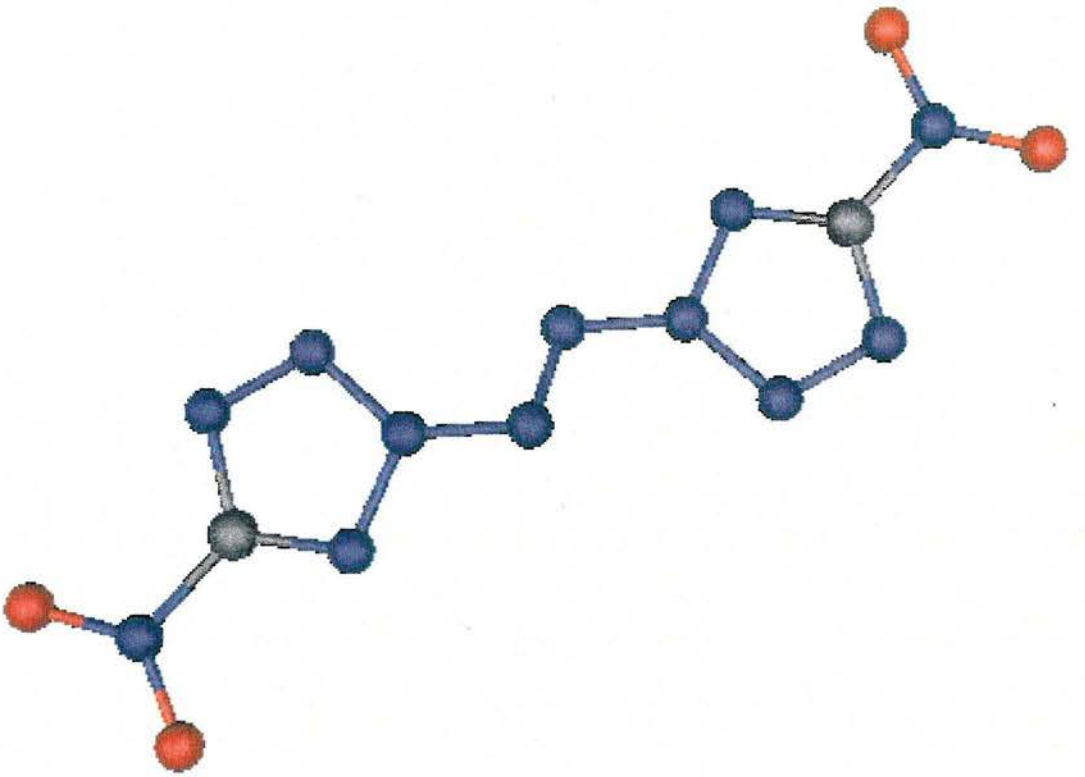


2

This reaction has a rather large 60 kcal/mol exothermicity. The barrier height for this decomposition must be determined, since given the complex changes involved, could be large and consequently involve a large barrier. However, **1** could also break an N-N single bond at either or both ends to form a mono- or di-azide, **3**:

N_3-C(NO_2)=N-N=N-N=C(NO_2)-N_3 **3**

This may still be an interesting species, and we will calculate its heat of formation, but it is probably considerably less energetic than **1**. It is also likely that loss of the central N_2 will be easier in **3** than in **1** and equally energetically favorable. Bottaro[37] has suggested that **4** (shown below), an isomer of **1**, may be more viable because it cannot undergo the analogous NN bond cleavage to form azides:



4

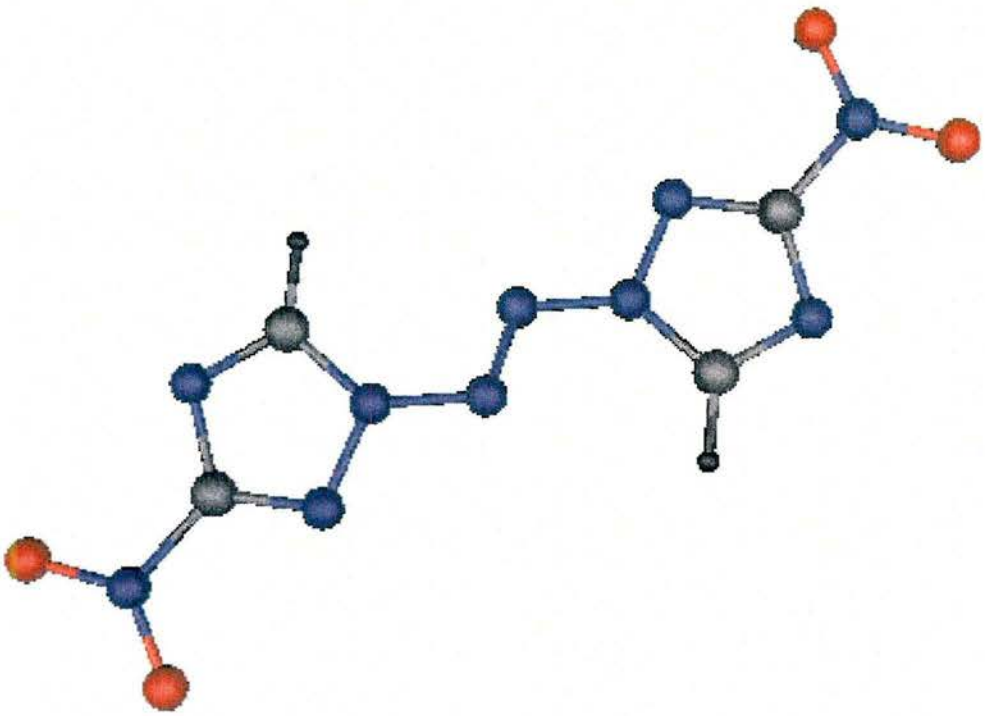
It is likely that **4** will have a heat of formation and I_{sp} that are comparable to those for **1**. The following calculations will be performed on this molecule: (1) To be consistent with the calculations on **1**, geometry optimization will be performed using second order perturbation theory (MP2) and the cc-pVTZ basis set; (2) The most likely breakdown products will be identified (see below), the corresponding geometries optimized, and the thermodynamic energy differences calculated; (3) For all of the exothermic decompositions, the corresponding transition states will be identified, the minimum energy reaction paths followed, and the dynamics examined; (4) Assuming the thermodynamic and kinetic calculations are optimistic, the heat of formation will be calculated in the manner described above and the I_{sp} calculated. The simplest, potentially exothermic decomposition one can imagine for **4** is the extrusion of N_2 from one or both of the 5-membered rings. Elimination of 2 N_2 would yield the unusual structure **4a**

$O_2N\text{-}C\text{-}(N)_6\text{-}C\text{-}NO_2$ **(4a)**

One would expect **4a** to be unstable to loss of two additional N_2 molecules, giving two nitronitriles, $O_2N\text{-}C{\equiv}N$. An alternative decomposition route for **4** would be to eliminate

successive O_2N-C≡N molecules, ultimately yielding N_6 which will then rapidly dissociate to 3 N_2.

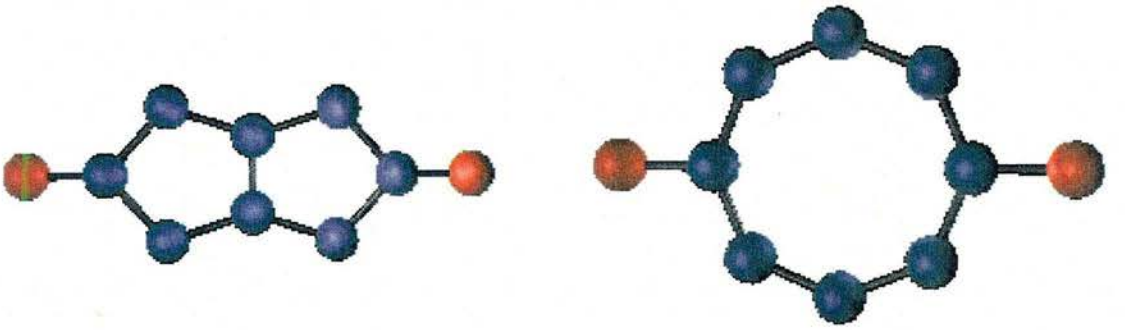
Although neither **1** nor **4** have yet been synthesized, the related compound, **5** below, has been made, and its crystal structure has been determined by Gilardi and Karle[38].



5

Using approximate additivity relationships, Bottaro and co-workers have estimated the heat of formation for **5** to be approximately 150 kcal/mol. Since this is a known compound, and since it is closely related to compounds **1** and **4**, it is important to determine a more accurate heat of formation and I_{sp} using the methods described above. We will also examine the effects of replacing the hydrogens with amino groups, since it is estimated that each such group will add about 47 kcal/mol to the heat of formation[37].

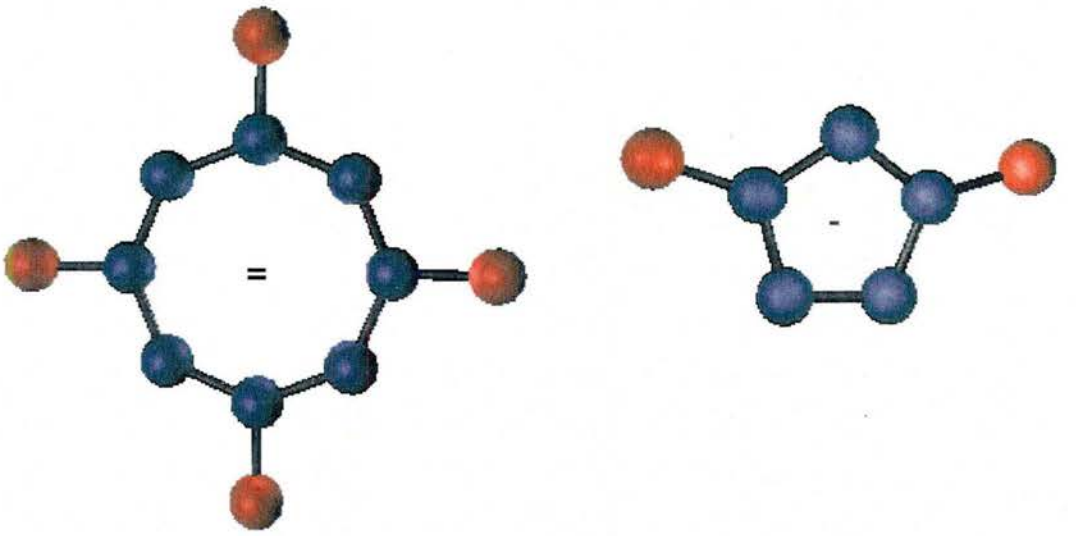
There are several additional N-O compounds that the SRI group have targeted for synthesis. In collaboration with Dr. Jerry Boatz at AFRL-Edwards, we will systematically analyze the molecular and electronic structures, mechanisms of formation, and heats of formation for these compounds. One of the most fascinating of these compounds is the proposed dimer of nitrosyl azide, N_3NO. The structure frequently written[37] for the dimer is structure (**a**) below:



(a) **(b)**

However, it is difficult to assign electrons using this arrangement in any sensible manner using standard Lewis structures. An alternative arrangement is the eight-membered ring, structure (**b**), in which there are alternating single and double NN bonds and formal single bonds to the oxygens. This structure does have a sensible Lewis structure and is also rather interesting since it contains an eight-membered nitrogen ring. This ring is isoelectronic with the well-known hydrocarbon cyclooctatetraene, so it is likely to be nonplanar. It will be very interesting to determine the actual structure of this dimer, its stability relative to the monomers, and possible pathways (in ground or excited electronic states) to dimerization and decomposition. As always, since N_2 is so stable, elimination of one or more N_2 molecules seems to be the most likely decomposition alternative to simple reversion to monomers. Initial calculations on these species will be performed using MP2/cc-pVTZ, however, close attention will be paid to the MP2 natural orbital occupation numbers, in order to monitor possible multi-reference character. The unusual electronic structure of **(a)** suggests significant configurational mixing in this species, not at all unusual in very high energy, metastable compounds. These compounds will also be excellent test cases for the new completely renormalized (CR)-CCSD(T) method in GAMESS[33]. The CR-CCSD(T) method can often account for considerable diradical character when normal CCSD(T), often thought of as state-of-the-art, cannot.

The dimer of nitrosyl azide is jut one example of a series of N-oxides which the SRI team is attempting to synthesize. The philosophy here is that the presence of the oxygen atoms may minimize nitrogen lone pair repulsions. Additional examples are the two cyclic anions shown below. The eight-membered ring structure is, of course, closely related to the N_3NO dimer, and one may consider both the neutral and dianionic species.



Two other NO anionic species whose syntheses are actively being pursued, and which we will characterize using the methods discussed above, are diaza- and triazanitrate:

It is important to emphasize that we will work closely with the SRI group, so that new calculations can be initiated as new promising targets are identified.

As noted in Section IA, we have worked with the AFRL-Edwards group to characterize the potential energy surface for $[AsF_6]^-[N_5]^+$. Christe et al. have prepared $[Sb_2F_{11}]^-[N_5]^+$, and the new counterion apparently considerably increases the stability of the $[N_5]^+$ species. An important point therefore must be the relative net energy requirements for the F^- transfer to $[N_5]^+$ from the two counterions. We will use second order perturbation theory geometry optimizations to determine the appropriate energy barriers and overall energy changes associated with the transfer. Ultimately, one clearly must understand the solid state properties of these compounds in order to fully understand their stabilities. We therefore plan to analyze the potential energy surfaces for small clusters of $X^-[N_5]^+$, $X = [AsF_6]^-$, $[Sb_2F_{11}]^-$, in order to enable studies by colleagues with experience in condensed matter theory (e.g., Thompson, Oklahoma State; Voth, Utah).

B. THEORY AND CODE DEVELOPMENTS

Nearly all of the QM calculations described above will require highly correlated wave functions and reliable atomic basis sets, as well as tools to study environmental effects. Because of the complexity and size of most of the species of interest, it will be important as well to maximize the efficiency of the calculations with highly scalable codes. Some

of the methodologies required, most notably reliable basis sets, are being developed by others and will simply be used by us. For example, in most cases the basis sets of choice will be those collectively referred to as correlation-consistent (cc) basis sets developed by Dunning and co-workers[39]. Single reference coupled cluster methods for closed shells have recently been added to GAMESS (General Atomic and Molecular Electronic Structure System) in collaboration with the Piecuch group (Michigan State)[33]. These new codes also include the completely renormalized (CR)-CCSD(T) method that has been shown to treat bond-breaking and diradical character much more reliably than the more traditional methods. Additionally, in collaboration with the Piecuch group, we are about to implement the equations-of-motion (EOM) coupled cluster methods for excited states, including the EOM-CCSD(T) method that is not readily available in other codes. The next steps in these developments by the Piecuch group will be to implement the analogous open shell codes and to derive and code the analytic gradients. Analytic gradients for a given CC method is the essential step in developing the density for that method and therefore all of the interesting response properties that are associated with the density. So, these new codes that are being developed by the Piecuch group and implemented into GAMESS by the ISU group will add significant new functionality to GAMESS. In the following paragraphs we focus on those new theory and code developments that will be carried out at Iowa State and that directly impact the HEDM program.

The Effective Fragment Potential: Solvent Effects and Liquid Properties. Solvent and other environmental effects are important for many of the applications discussed above, in particular the study of ionic liquids. In addition, there are many problems of current interest to the Air Force that require an understanding of the liquid-surface interface. In collaboration with Prof. Jensen (U. Iowa), we will continue the development and implementation of new techniques to treat solvent effects and liquids, based on the effective fragment potential (EFP) method[9,40,41]. Indeed, the ultimate goal of the development of the suite of EFP methods is to construct model potentials from first principles that are able to address the broad range of environmental effects.

Our general approach to solvent effects consists of three layers. The innermost layer consists of a fully quantum mechanical (QM: *ab initio* or DFT) treatment of the "solute" plus n solvent molecules (e.g., waters), where n will typically be a small number, perhaps determined by the role particular solvent molecules might play in making or breaking new bonds. The solute may be a single molecule of interest or a reacting system. The latter is important, since we plan to study environmental (e.g., condensed phase) effects on reaction mechanisms and dynamics. The second layer consists of EFP molecules: a collection of m explicit solvent molecules in the immediate vicinity of the solute (compound or reacting system). The internal fragment geometries are currently held fixed, but the positions of these solvent molecules may be optimized. One may think of m + n as the inner solvation layer. The third, outermost layer is some representation of the bulk (continuum) solvent.

The interactions between solute (QM) and solvent (EFP) molecules are treated by adding *one-electron terms* to the QM Hamiltonian to represent these interactions[9,40,41]. For EFP-

EFP interactions, an analogous set of interaction energies are derived. For each QM-EFP and EFP-EFP interaction term, energy gradients are derived and coded to enable geometry optimizations, reaction path following and dynamics calculations in the presence of solvent or indeed for the solvent (liquid) alone. In general, such a potential may be expressed as

$$E_{int} = E_{coul} + E_{ind} + E_{er} + E_{ct} + E_{disp} + E_{ho},$$

where these terms represent, respectively, Coulomb, induction (polarization), exchange repulsion, charge transfer, dispersion and higher order interactions. The Hartree-Fock, GVB or MCSCF levels of theory contain the first four terms that are determined as follows[9]:
- $\mathbf{E_{coul}}$ is treated by a *distributed* multipolar expansion[42] through octupoles, with expansion points at the atom centers and bond midpoints. The entire expansion is damped by a screening term that accounts for the effect of overlapping charge densities as the distance between molecules decreases.
- $\mathbf{E_{ind}}$ is treated in a self-consistent manner using tensor sums of localized orbital polarizabilities located at the centroid of each bond and lone pair of the fragment. Both E_{coul} and E_{ind} are determined from QM monomer calculations.

In the EFP1 method, once $E_{coul} + E_{ind}$ have been determined for a given monomer (e.g., H_2O), $\mathbf{E_{er} + E_{ct}}$ are obtained by a fitting procedure. One determines the SCF dimer interaction energy for a large number of geometries. For water, ~200 dimer points were obtained by choosing several water-water orientations and then several O-O distances for each orientation. At each dimer geometry $E_{coul} + E_{ind}$ is subtracted from the total SCF interaction energy, and the remainder ($E_{er} + E_{ct}$) is fitted to gaussian (EFP-EFP) or exponential (QM-EFP) functions that are centered at the atom centers and the center of mass. Note that this formulation of the EFP method permits systematic improvements in the accuracy, by the addition of higher order, but still easily calculated one-electron, terms to the QM Hamiltonian. The EFP method for water reproduces HF results with high accuracy for geometries, vibrational frequencies, energy differences, barrier heights, and even reaction paths[13,43]. In order to incorporate some correlation into the method, a DFT-based EFP1 method has recently been implemented[12] using the B3LYP functional. The fitted term now presumably contains some short range correlation in addition to $E_{er} + E_{ct}$, and of course $E_{coul} + E_{ind}$ are now obtained with DFT.

The next step in the development of EFP1 for water will be to extend the method to the MP2 level of theory, in order to fully incorporate dispersion effects. $E_{coul} + E_{ind}$ will be determined in a manner similar to that described above for SCF and DFT, except making use of the MP2 multipoles and polarizabilities. The fitting procedure will be split into two pieces. The first, again representing $E_{coul} + E_{ind}$ will be done as before using the HF fit. Then the sum $E_{coul} + E_{ind} + E_{er} + E_{ct}$ will be subtracted from the each of ~200 MP2 $(H_2O)_2$ interaction energies. This remainder, largely E_{disp}, will then be fit separately to obtain the dispersion function, multiplied by a damping term that ensures $E_{disp} \rightarrow 0$ at short distances (e.g., $1\text{-}e^{-aR}$). The simplest approach is to assume that one only needs the C_6 term in the dispersion expansion[42], however, we will explore the possibility that

higher order terms (e.g., C_8) might improve the fit to MP2 interaction energies. The introduction of E_{disp} and the corresponding gradient expression will also require the derivation and implementation of new integrals in the EFP code, since the Rys polynomials will not be applicable. However, these will still be simple one-electron integrals.

While the determination of the E_{coul} and E_{ind} are easily automated and need only be done once for a given solvent, the fitting process for $E_{er} + E_{ct}$ and E_{disp} is a significant bottleneck, since it must be repeated for each solvent of interest. For more complex solvents the number of necessary dimer points may be very large. Therefore, in addition to the EFP1 method for H_2O, we have begun to explore a more general, "first principles" EFP2 method that does not rely on fits to QM data. This has already been accomplished for the exchange repulsion between two fragments[44], by making use of an expansion in the overlap matrix, terminated at second order. By representing the wavefunctions on the interacting molecules by localized molecular orbitals, this simple method, that requires only the evaluation of one-electron integrals, provides a very accurate representation of the exact intermolecular exchange energy. This method has now been incorporated into the EFP code, complete with analytic gradients, and it has been successfully tested for many solvents[9]. The extension of this method to the QM-EFP exchange repulsion has also been completed and incorporated into GAMESS.

So, the current EFP2 method includes $E_{er} + E_{ct} + E_{er}$ with no fitted parameters. *The next steps* will be to *first* derive and code the analytic gradient for the QM-EFP E_{er} interaction. *Second*, we will develop an independent term for E_{disp}. *Dispersion* will be introduced into EFP2 initially by following the lead of Amos et al[45-47], by developing and implementing a distributed LMO model,

$$E_{Disp} = \sum_{k\in A}\sum_{j\in B}\sum_{\alpha\beta\gamma\delta}^{x,y,z} T^{kj}_{\alpha\beta} T^{kj}_{\gamma\delta} \int_0^\infty d\nu \alpha^k_{\alpha\gamma}(i\nu)\alpha^j_{\beta\delta}(i\nu) \qquad (1)$$

where, for example, $\alpha^k(i\nu)$ is the frequency-dependent polarizability of LMO k at imaginary frequency ν and T^{kj} is the field gradient (which scales as r^{-3}). The integral will be computed by numerical quadrature using ~20 points as suggested by Stone.[87] Thus, the frequency-dependent polarizability tensors will be pre-computed for each LMO at ~20 frequencies using time-dependent (TD) DFT[46,47], and stored as part of the EFP. $\alpha^k(i\nu)$ tends to zero with increasing frequency, so the proper frequency range can easily be determined by systematically decreasing the frequency. TD DFT is expected[47] to predict $\alpha^k(i\nu)$ to an accuracy of 10-20%. Since the $\alpha^k(i\nu)$ need only be calculated once for a given molecule, this approach can be tested for small molecules (e.g., H_2O, NH_3) using our new fully parallel Full CI code[48] and the sum over states (SOS) method. This will provide exact results for a given atomic basis and will therefore calibrate the TD DFT method that must be used for larger molecules of interest. Since charge penetration effects can significantly damp the dispersion energy[42] at short range, we will initially explore the damping approach introduced by Thole,[49] in which the field gradient is damped by modifying its functional form to reflect an approximate charge distribution shape. While Thole's approach introduces empirical parameters, we will explore the use

of the SGO (spherical Gaussian orbital) approximation[9,44] to introduce overlap-dependent parameters that can be evaluated directly.

The QM-EFP dispersion energy analogous to Eq (1) can be derived by a multipole expansion of EFP B only,

$$E_{Disp} = \sum_{i\in A}\sum_{m\in A}^{vir}\sum_{j\in B}\sum_{\alpha\beta}^{x,y,z}\langle i|\hat{T}_\alpha^{i\,j}\hat{T}_\beta^{i\,j}|m\rangle\int_0^\infty d\nu\frac{(\varepsilon_m-\varepsilon_i)\alpha_{\alpha\beta}^j(i\nu)}{(\varepsilon_m-\varepsilon_i)^2+\nu^2} \qquad (2)$$

The integral is over orbitals on QM atom A and ε_i is the energy of orbital i. Thus, the dispersion energy is computed using converged SCF orbitals in analogy with the MP2 energy. Since both equations only involve one-electron integrals they can be computed at trivial expense compared to the MP2 energy of molecule A. The damping contribution will be incorporated by modifying the electric field operator as described above. *The energy and gradient expressions will be derived, coded and tested as part of the proposed research.*

Third, Jensen[50] has derived an expression for E_{ct}, using the same SGO approach that has been so successful for E_{er}. The gradient for this term will be derived, and the energy + gradient tested for accuracy and efficiency. A proper treatment of E_{ct} will be especially important for ionic interactions. So, this will be a key development for our ability to treat ionic liquids.

The EFP method has already been interfaced with MCSCF wavefunctions in GAMESS, so qualitative studies of excited state solvent effects are already possible[51]. Nonetheless, an interface with the CI code is desirable for more accurate excited state solvation studies. Webb[52] has very recently implemented a distributed parallel CI singles method into GAMESS, including analytic gradients. The gradients provide us with the Hellmann-Feynman term for the CI first order density matrix, so we are now in a position to develop a CI-EFP interface for treating excited state solvent effects, including geometries, reaction paths, and dynamics. These capabilities will be implemented during the next grant period. A longer term goal is to derive and implement gradients for multi-reference CI and EOM-CC methods, so that their first order density matrices will be available to interface with EFP2.

In order to treat extended systems, such as those to be encountered in the ionic liquids project, it will be necessary to develop both Monte Carlo and molecular dynamics methods with periodic boundary conditions and long-range cutoffs. A Monte Carlo (with basin hopping) simulated annealing code has been implemented and tested on water clusters[13] and simple organic acids[53]. For the study of ionic liquids, we will need to extend this code to include periodic boundary conditions, and either Ewald sums or FMM for long-range cutoffs. Since we have already developed FMM methods[17,18], this will be the first approach, however, Ewald sums will also be coded. This new MC code will then facilitate the study of phase changes and melting of ionic liquids. We have also implemented an EFP1/MD code, using periodic boundary conditions (PBC), the minimum image convention (MIC) and quaternions to deal with the internally frozen geometries. A fully QM MD code is also in progress. *As part of the proposed* research, we will extend this code to the new EFP2 method, complete with dispersion and charge

transfer terms, and then implement Ewald sums to deal with long-range interactions. The combination of MC and MD methods will allow us to simulate bulk condensed phase behavior. Once the new QM/EFP interaction terms (dispersion, charge transfer) have been derived and coded, the Monte Carlo code will be extended to QM/EFP2 calculations. Likewise, once analytic gradients are derived and coded for each of the QM/EFP2 interaction terms, the MD code will be adapted to QM/EFP2 calculations. This combination of techniques will facilitate the study of the decomposition mechanisms of ionic liquids in the presence of the extended system.

Scalable Computing and Linear Scaling Methods. The computer time requirements for *ab initio* calculations increase dramatically with the size of the system to be treated, even at the SCF level. Even model potentials, which require orders of magnitude less computation time than *ab initio* computations for an energy + gradient run, can be extremely time-consuming if one requires tens of thousands of points in a molecular dynamics (MD) or Monte Carlo simulation. Two very successful approaches for solving this problem in our group have been the development of new methods for scalable, distributed parallel computing and new approaches for linear scaling algorithms. Much of the parallel developments in GAMESS[54] over the past several years has been supported by a separate DOD CHSSI software development grant that will almost certainly not be renewed beyond the termination date of 12/04. That grant has enabled us to develop the distributed data interface (DDI)[55,56] and thereby implement algorithms for MP2 and UMP2 energies + gradients, and ZAPT2 and MRMP2 energies, that scale essentially perfectly up to 512 processors on systems like the T3E and to 32-64 processors on UNIX or Linux clusters. A new DDI-based scalable CASSCF analytic Hessian code has just been completed[57] and appears to scale very well. Analogous codes are under development for ZAPT2 gradients and CASSCF energies + gradients.

The *main focus regarding parallel code development for the research proposed here* will be on scalable QM/EFP methods discussed above, and the linear scaling methods discussed below. The over-riding motivation is to enable us to use larger QM regions in the QM/EFP calculations, and to perform simulations using larger EFP regions. The one addition is the need to develop scalable gradients for state-averaged CASSCF calculations, because this method is essential for the calculation of non-adiabatic matrix elements, such as spin-orbit coupling and vibronic (derivative) coupling. The latter could well be important for the study of some of the potential energy surfaces of polynitrogen species.

As part of the CHSSI program, we have developed codes for EFP1/HF that scale very well to 32 processors, as long as one sensibly grows the size of the system with the number of processors. This effort benefited greatly from the efforts of Heather Netzloff, a student who was supported entirely by her own fellowship funds throughout her graduate career. The analogous code for EFP1/DFT should now be straightforward, and this will be our *first goal*. The parallel code for EFP1/MP2 should be similar, as the only completely new terms will be those for the dispersion energies and gradients. Once parallel codes for all of the EFP1 variants have been completed, a parallel code for the EFP2 method will be developed. Since the Coulomb and polarizability terms will be

analogous to those in EFP1, the focus will naturally be on the exchange repulsion, dispersion and charge transfer energies and corresponding gradients.

The discussion in the previous paragraph focused entirely on developing parallel EFP codes, but developing the analogous codes for the EFP-QM interaction terms is at least as important. One would like, for example, to have the capability to perform Monte Carlo or molecular dynamics simulations on EFP arrangements in the presence of a QM "solute". In order to make such a calculation feasible for a reasonable number of structures, one needs all EFP-EFP and EFP-QM terms to be calculated as efficiently as possible. Given our success in developing such codes for QM and EFP separately, there is little doubt that this will be a successful effort. Several of the QM methods in GAMESS (e.g., CCSD(T), MRMP2) do not yet have analytic gradients. Fortunately, we have recently developed a group-based extension of DDI (GDDI)[58,59] in which numerical derivatives become trivially parallel in a coarse-grained sense by having each function evaluation performed on a different node. If the function itself exists as a parallel code in GAMESS (e.g., MRMP2), and if the nodes are SMP nodes, the multi-level parallelism can be exploited. At present, GDDI can only be applied to fully QM calculations. As part of the proposed research, we will extend this very useful approach to EFP calculations.

Building on beautiful work by the Head-Gordon[60] and other[61] groups, we have previously developed an optimized linear scaling fast multipole (FMM) method for the Coulomb term in both HF and DFT[17,18]. The novelty of this approach is that it is formulated in such a manner that one can identify a small number of parameters that can be easily optimized in an iterative manner to optimize the linearity of the scaling. The desired accuracy for the entire calculation is an input parameter. A replicated data parallel code was developed for this method that scales moderately (factor of six on eight processors for a model problem). *Several new features will be developed as part of the proposed research*: (1) Analytic derivatives will be derived and coded, to enable geometry predictions, reaction path following and the evaluation of vibrational frequencies via semi-numerical Hessians; (2) Flexibility will be introduced into the method so that accuracy in some regions of an extended system (e.g., a protein) that are far from the chemical "action" are allowed to be lower than the accuracy required where the chemistry is taking place; (3) The method will be extended to MCSCF wavefunctions, since many problems of interest to us are inherently multi-configurational, and subsequently to second order perturbation theory methods; (4) Distributed data parallel codes will be developed for all levels of our linear scaling *ansatz*. All of these techniques will be incorporated into the 2-D PBC code we are already developing to treat the chemistry that occurs on metal surfaces. This will provide the essential ingredients for the study of heterogeneous catalysis of ionic liquids decomposition on metal catalysts.

Thermodynamic properties. The availability of accurate methods for predicting thrmodynamic properties, such as heats of formation, is important in order to accurately estimate the specific impulse. The most popular such methods are the G2[35] and G3[36] methods developed by Pople and co-workers. One limitation of these methods is that they are applicable only to species that are adequately described by single configuration

wavefunctions. This is a serious limitation for many species of interest to the HEDM program, since such species frequently have unusual bonding arrangements and are therefore not well described by single configuration wavefunctions. We have therefore developed, in collaboration with the Radom group, multi-reference analogs of the G2 and G3 methods[19]. In these methods, the single configuration Hartree-Fock wavefunction is replaced by a full valence MCSCF wavefunction, single reference MP2 is replaced by multi-reference second order perturbation theory (MRMP), and QCISD(T) is replaced by multi-reference CI (MRCI). The method has been tested on the G2-1 test set, with accuracy similar to that of the original single configuration-based methods[62].